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**ARPA Coupling Program on
Stress-Corrosion Cracking
(Eighth Quarterly Report)**

E. P. DAHLBERG (General Editor)

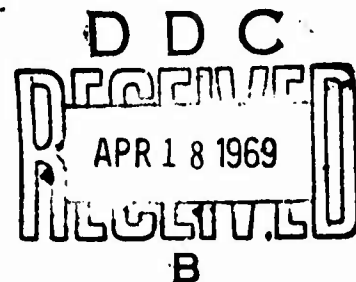
*Physical Metallurgy Branch
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ABSTRACT

This report contains a compilation of abstracts from recently published reports and journal articles generated under the ARPA Coupling Program on Stress-Corrosion Cracking, ARPA Order 878. The abstracted reports are from work done at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory. Selected abstracts of articles from outside the ARPA program in the field of stress-corrosion cracking and a diary of events are also included.

STATUS

This is a progress report; work is continuing.

AUTHORIZATION

NRL Problems 61M04-08
63M04-08A
ARPA Order 878 and
RR 007-08-44-5512

INTRODUCTION

The problem area of stress-corrosion cracking (SCC) in structural materials leading to failures in engineering structures has been of continuing concern to the Department of Defense and to other users of structural materials. Although considerable progress had been made in the field of corrosion, insufficient information was available to reach reliable conclusions on the phenomena of SCC and on the mechanisms involved. In addition, a definite weakness existed in the educational field relative to academic involvement and effort in developing suitable curricula to achieve reasonable understanding and agreement on the basic causes of SCC and on the resulting failures in engineering structures. Without the development of reliable mechanism(s) and understanding of the factors involved in SCC phenomena, development and application of high strength alloys for reliable service in various environments can proceed only empirically.

In order to bridge the gap in fundamental knowledge needed to understand and to cope with the problem of SCC and to apply this knowledge to obtaining improvement of SCC resistance in existing and newly developed high strength alloys, the Advanced Research Projects Agency (ARPA) of DoD established a project on SCC under ARPA Order 878. This project, a broadly based interdisciplinary experiment, involves a coupling program between academic, industrial, and Government laboratory participants. The technological goal is to learn how to improve high strength structural alloys with respect to their resistance to SCC under various environmental and stress conditions, or at least learn how to "live with" the alloys which we haven't been able to improve sufficiently.

Academic disciplines needed in the attack on the SCC problem area were considered to include: modern physical metallurgy, surface chemistry and electrochemistry, physics of surfaces, continuum mechanics as applied to fracture, advanced techniques of analysis, and development of environment-metal reaction theory. The industrial participant affords a means of amplifying a Government

laboratory's in-house capability without an increase in in-house staff. The Government laboratory's role was to exercise overall project direction, to provide direction guidance as to DoD needs, and to conduct basic and applied research.

The academic participants and their principal discipline areas have been as follows:

a. Carnegie-Mellon University -- Advanced physical metallurgy and electrochemistry.

b. Georgia Institute of Technology -- Surface physics and physical metallurgy.

c. Lehigh University -- Surface chemistry, metallurgy, and fracture mechanics.

d. American University -- Solution chemistry and electrochemical effects (in aluminum).

e. University of Florida -- Electrochemistry, particularly in conducting Pourbaix-type analyses for alloy systems.

The Boeing Company, the industrial partner, develops standard test methods and characterizes SCC properties of advanced high strength alloys; provides technical guidance in areas of special competence; and conducts a limited amount of basic research in related areas.

The Naval Research Laboratory is the Government laboratory participant. Its research and discipline areas are: physical metallurgy, electrochemistry, surface chemistry, solution chemistry, surface physics, and fracture mechanics.

In addition, NRL identifies relevant military hardware needs in the area of SCC.

The technical reporting system includes the following:

Detailed technical progress from each project participant is published twice yearly in the quarterly report series. The technical progress report is organized into three main categories: Titanium, Steel, Aluminum. Each main category is further divided according to material classification and to research discipline. The individual progress reports are sent to and edited by category editors who in turn submit the edited progress reports to NRL for assembly into the quarterly report and publication as an NRL report. The remaining two quarterly reports contain (1) abstracts of newly published reports of project sponsored research, (2) a chronological list of titles of all ARPA-generated reports, and (3) selected abstracts of reports and journal articles of work related to SCC outside the ARPA project. A final item is a diary of events section.

A. ABSTRACTS OF ARPA-GENERATED
MANUSCRIPTS AND REPORTS

The Boeing Company

1. A. K. Mukherjee, "The Possible Role of Hydrogen in Stress-Corrosion Cracking of Titanium Alloys," Boeing Document No. D6-23621, September 1967

The various mechanisms that have been put forward to explain stress-corrosion cracking are briefly summarized. The experimental observations of stress-corrosion cracking in titanium alloys in widely different environments are discussed. Evidence from the literature for and against the possibility that hydrogen plays a role in the stress-corrosion cracking of titanium alloys is documented. An experimental approach is outlined in an attempt to establish if environmental cracking in titanium alloys in specific environments is due mainly to a stress-corrosion mechanism or to a process similar to hydrogen embrittlement.

2. C. S. Carter, "Crack Extension in Several High-Strength Steels Loaded in 3.5% Sodium Chloride Solution," Boeing Document No. D6-19770, November 1967

The morphology of crack growth was determined on precracked, notched bend specimens of 300M, H11, Maraging 250, 4330V, 9Ni-4Co-0.30C, and 9Ni-4Co-0.45C (martensitic and bainitic) steels four-point loaded in 3.5% sodium chloride solution. Crack extension from the tip of the fatigue precrack was either by a single crack that propagated along the fatigue crack plane (Type 1 cracking) or by two divergent cracks that propagated at an angle to the fatigue crack plane (Type 2 cracking). The 4330V, 9Ni-4Co-0.30C, and 9Ni-4Co-0.45C (bainitic) showed either Type 1 or Type 2 cracking, depending on the initial stress-intensity level K_{Ii} . The remaining steels exhibited only Type 1 cracking. The state of stress had a

significant effect on the morphology of Type 2 cracks. The morphology suggests that Type 2 cracking is a result of environmental cracking along crack-tip plastic zones. The influence of yield strength on K_{Isc} can be described by an empirical expression.

3. C. S. Carter, "Terminal Fracture of Titanium Alloys Containing Stress-Corrosion Cracks," Boeing Document No. D6-19771, May 1968

Approximately one hundred precracked notch bend specimens of Ti-6Al-4V and Ti-4Al-3Mo-1V, previously sustain loaded in 3.5% sodium chloride solution, have been examined. The conditions for complete separation of the specimens were determined. In general, this occurred when the stress intensity at the border of the extending stress-corrosion crack reached the plane strain fracture toughness K_{Ic} . Observed deviations from this behavior were primarily attributed to crack length measurement difficulties. The fatigue precrack in specimens loaded to stress intensity levels below the threshold stress intensity level K_{Isc} was not affected by the environment, i.e., there was no blunting.

4. J. C. Williams, R. R. Boyer, M. J. Blackburn, "Influence of Microstructure on the Fracture Topography of Titanium Alloys," Boeing Document No. D6-23620, June 1968; to be published in an ASTM Special Technical Publication

A survey is presented of the fracture topography observed in titanium and titanium alloys. Ductile fracture by microvoid nucleation, growth, and coalescence is of widespread occurrence in these alloys. It is usually possible to qualitatively relate the dimple size to the macroscopic ductility of the alloy. Titanium alloys may be embrittled by alloying additions that, in most cases, lead to a fine dispersion of second-phase particles. In alpha phase alloys, this brittleness

is associated with cleavage fracture. However, beta phase alloys, which exhibit cleavage-like macroscopic behavior, show evidence of small dimples when observed using a microscope. Environment often dramatically affects the fracture behavior of titanium alloys, producing low-energy cleavage-like failures in alpha and beta phases, which are normally ductile. We attempt to relate observations of fracture behavior and topography to structural and environmental factors.

5. R. E. Curtis, "Relationship Between Composition, Microstructure, and Stress-Corrosion Cracking in Titanium Alloys," Boeing Document No. D6-23716, September 1968

Four alpha titanium alloys and eleven alpha-beta titanium alloys have been characterized to relate phase composition and associated microstructure to stress-corrosion cracking. Of these alloys, only a low interstitial, commercially pure alpha alloy, Ti-50, was immune to SCC. Addition of oxygen or aluminum and tin promoted susceptibility in the alpha phase by restricting slip to a single set of planes. Formation of ordered domains of $Ti_3(Al,Sn)$ further restricted slip and increased stress corrosion susceptibility. Thermomechanical treatments which reduced alpha grain size or increased dislocation density improved stress corrosion resistance by limiting the slip length. Alloying with molybdenum and/or vanadium increased strength and often improved stress corrosion resistance by stabilizing the ductile beta phase. However, precipitation of a fine dispersion of alpha or omega in beta caused embrittlement and reduced the stress corrosion threshold. Intermetallic compound formation in alloys containing copper or silicon similarly promoted susceptibility. Thermomechanical processing of Ti-4Al-4Mo-2Sn-0.5Si limited the embrittlement by refining transformed beta.

6. D. N. Fager, "Methanol Cracking of Titanium-8Al-1Mo-1V," Boeing Document No. D6-23717, September 1968

A comparison is made between methanol and salt solution cracking of Ti-8Al-1Mo-1V. Stress-corrosion tests conducted on material with an extreme preferred orientation demonstrated that cracking in methanol must occur on or near the basal plane similar to cracking in salt solution. It is indicated that, although cracking occurs at a lower stress level in methanol, some step in the cleavage process is slower than in salt solution.

Carnegie-Mellon University

1. R. P. M. Procter and H. W. Paxton, "Stress-Corrosion of the Aluminum Alloy 7075-T651 in Organic Liquids," submitted to ASTM for publication

It has been shown that stress-corrosion cracks will propagate from a fatigue-precrack in 7075-T651 aluminum alloy exposed to various organic environments; stress-corrosion cracks will not however, initiate in smooth specimens. Evidence is presented which indicates that the crack propagation is probably not due to traces of water adsorbed in the oxide film at the crack tip or in the environments. The stress-corrosion crack growth rate was measured in ethanol and carbon tetrachloride as a function of the plane-strain stress-intensity factor K_I . A linearly increasing relationship was observed and from these results, values of K_{Isc} for each environment were estimated. The results of a fractographic analysis of the fracture surfaces are described. Evidence is presented to show that some limited dissolution of aluminum in the environments occurs and it is suggested that, as with aqueous stress-corrosion of aluminum alloys, an electrochemical reaction is involved in the cracking.

2. J. Y. Choi and P. G. Shewman, "Diffusion of Hydrogen in Steel Exposed to Water," submitted to AIME for publication

The diffusion of hydrogen through a fully-annealed pure iron specimen exposed to distilled water was studied using a mass spectrometer; hydrogen diffuses into iron only when it is in contact with water. The diffusion increases with temperature and is accelerated by abrading the iron surface. A "one-side" decay profile fitted the experimentally observed decay curve better than a "both-sides" decay profile. Abrasion and the hydrogen ion concentration in a buffered solution did not affect the diffusion coefficient of hydrogen but increased the hydrogen concentration at the iron/water interface. The diffusion coefficient of hydrogen in iron in the range 10-100°C is given by:

$D = 2.23 \times 10^{-3} \exp\left(-\frac{3,100}{RT}\right)$. Permeability of hydrogen through fully-annealed pure iron exposed to distilled water without abrasion is given by:

$P = 7.2 \times 10^{-2} \exp\left(-\frac{13,000}{RT}\right)$. An atomic model for interpreting the mechanism of hydrogen diffusion in iron and the surface corrosion of iron in water is presented.

3. R. D. Townsend and A. J. DeArdo, Jr., "The Effect of Microstructure on the Mechanical Properties and Stress-Corrosion Resistance of an Al-Zn-Mg Alloy," submitted to ASTM for publication

The role of microstructure in controlling the susceptibility of aluminum alloys to stress-corrosion cracking has been the subject of wide controversy. At the center of this controversy is the actual role played by the precipitate free zones (P.F.Z.s) which occur adjacent to the grain boundaries. Several authors have proposed that such P.F.Z.s have deleterious effect on stress-corrosion cracking while others consider

these regions to play no part in the phenomenon. The purpose of this investigation was to investigate the effect of the P.F.Z.s on the mechanical properties and the susceptibility to stress-corrosion cracking of a high purity Al-6.8% Zn-2.3% Mg alloy. Heat treatments were developed to vary the width of the P.F.Z. and also to control the type and dispersion of precipitates within the grain interiors, after aging treatments above the G.P. zone solvus temperature. The results strongly indicate that the existence of a P.F.Z. does not have a first order effect in controlling either the mechanical properties or the stress-corrosion resistance of this alloy, but that variations in these properties are predominantly caused by changes in the type and distribution of matrix precipitates.

Georgia Institute of Technology

1. Panagiotis Kalofonos, Thesis for Master's degree - "Stress Corrosion Cracking in Almar 362 Mar-aging Stainless Steel," October 1968

The object of this investigation was to study stress-corrosion cracking in Almar 362 mar-aging steel.

Time to failure as a function of applied stress was determined for numerous heat treatments and for various applied external currents. Material aged at higher temperatures was found to be less susceptible to stress corrosion cracking, compared to material aged at the lower temperatures. This steel had very good resistance to cracking when aged at about 1150°F.

When the Almar 362 was austenitized, cold rolled and then directly aged, the significant increase in tensile strength was accompanied by the highest susceptibility for hydrogen embrittlement cracking. This susceptibility diminished with decreasing strength of the steel.

Potential-time curves showed that when stress cracking occurred in a chloride solution containing acetic acid or SeO_2 , an impressed anodic current of a few mA markedly increased the life of the material, whereas an impressed cathodic current decreased the time to failure. This is strong evidence to support a conclusion that in such media the Almar 362 fails by hydrogen embrittlement cracking. These corrodents were also found to play an important role in reducing the notch strength of this steel.

Metallographic and electron microscopy data indicated no difference between anodic and cathodic fractures.

2. G. W. Simmons and E. J. Scheibner, "Order-Disorder Phenomena in the Surface of α -Titanium-Oxygen Solid Solutions," submitted to ACTA Met.

During low energy diffraction (LEED) studies of α -titanium surfaces an order-disorder reaction was discovered when oxygen was present in the surface. The oxygen solid solutions were formed by the reduction of a thin oxide layer by the titanium at 750°C .

Three phases were observed, a random solution (TiO_{0+x}) and two ordered solutions ($\text{Ti}_2\text{O}_{1-y}$) and (Ti_3O). Superlattice reflections observed in the LEED patterns and in the intensity distributions are consistent with the structures reported elsewhere for these solutions.

An order-disorder transition ($\text{Ti}_2\text{O}_{1-y}$ TiO_{0+x}) was observed at $475^\circ\text{C} \pm 50^\circ$. The lattice along the c-axis was shown to be greater for the ordered ($\text{Ti}_2\text{O}_{1-y}$) than for the disordered (TiO_{0+x}) solution. Similar measurements in the a-direction are planned, but have not yet been made.

The Ti_3O structure was observed in a temperature range of between 200°C and 300°C . This structure was found to be unstable outside these temperature limits. No significant lattice parameter changes were observed for the reaction ($\text{Ti}_2\text{O}_{1-y}$ - Ti_3O).

There is no clear evidence that these order-disorder transitions occur in bulk solid solutions. It is proposed, therefore, that this phenomena is restricted to the surface region.

3. D. A. Mauney and E. A. Starke, Jr., "Explanation of the Cleavage Plane Observed in Stress Corrosion Cracking of α Phase Titanium-Aluminum Alloys," submitted to Corrosion for publication

An explanation of the stress corrosion cleavage plane observed in α phase titanium-aluminum alloys which have failed in salt water or methanol environment is discussed in terms of blockage of the major slip systems by aluminum and/or hydride formation. This blockage allows slip to occur on a less prominent system which results, when considering the Stroh fracture theory, in the observed cleavage plane.

4. R. F. Hochman and H. E. Grenga, "A Review of Field Ion and Field Emission Microscopy Studies of Corrosion," submitted to ASTM for publication

The development of field emission and field ion microscopy provide two powerful new tools to study surface phenomena. Field Emission Microscopy (FEM) studies have provided data on surface work function measurements and surface migrations of oxygen, hydrogen, carbon monoxide, etc. Basic knowledge of adsorption characteristics have resulted from the work of several scientists in this area. Most recently FEM studies of stress-environment interactions have been reported. Field ion microscopy (FIM) has also provided new information on oxide formations as well as gas and mercury corrosion effects. These studies will be reviewed and in-progress work will be discussed on the effect of hydrogen on metals.

Lehigh University

1. W. A. Spitzig and R. P. Wei, "Fatigue-Crack Propagation in Modified 300-Grade Maraging Steel," Journal of Engineering Fracture Mechanics, Vol. 1, 1968 (in press)

Fatigue-crack-propagation studies were performed on an 18Ni (300-grade) maraging steel at room temperature in dry and humid argon environments (atmospheric pressure) to examine the effect of moisture on the rate of fatigue-crack propagation and on the fracture path through the microstructure. The results showed that the rate of fatigue-crack propagation was increased by about 30 percent by moisture in the argon.

Fractographic analyses showed that the crack path in the dry-argon atmosphere was transgranular. In the humid-argon atmosphere, the crack path was predominantly transgranular with respect to prior austenite-grain boundaries, but appeared to be partly intergranular with respect to subboundaries. The fracture surfaces of the specimens were covered with fatigue striations regardless of the testing environment, an indication that the mechanism of crack growth was similar in both environments, even though the fracture surfaces of the specimens fatigued in dry argon were rougher. Therefore, although moisture in the argon environment accelerated crack growth by about 30 percent, it apparently did not change the mechanism of crack growth. Evidently the effect of moisture in the environment is to promote striation-type crack growth along paths such as subboundaries. A comparison of fractographic results with those of previous work on hydrogen-accelerated fatigue-crack growth in 250-grade maraging steel indicates that in 300-grade maraging steel the increased rate of fatigue-crack growth in the humid environment is not hydrogen-induced.

2. R. D. Iyengar, V. V. Subba Rao, and A. C. Zettlemoyer, "Electron Spin Resonance Studies of the Interaction of O_2 , NO_2 , NO , N_2O and Cl_2 with Zinc Oxide," to be published in Surface Science, December 1968

An electron spin resonance study of the surface interaction of zinc oxide with oxygen, oxides of nitrogen (NO_2 , NO and N_2O) and chlorine was made. Characteristic spectra obtained following adsorption of NO_2 and NO were analyzed and attributed to rigidly adsorbed neutral molecules. Confirmation of the assignment was provided by the use of the respective adsorbates enriched in ^{15}N ($I = 1/2$).

When vacuum-outgassed ZnO was exposed at 25° to N_2O , NO or Cl_2 at low pressures, the complex signal at $g \sim 1.96$ was replaced by two signals with g values very close to 1.96. The origin and identity of the signals are discussed. A new signal at $g = 2.015$ was produced by treatment of ZnO at 25° with NO_2 or Cl_2 . The same signal could also be obtained on heating ZnO with small amounts of NO or N_2O in the range $250-350^\circ$. The species responsible for this signal was not identified.

3. Kamil Klier, "A Geiger-Muller Counter for Ultrahigh Vacuum Systems," Review of Scientific Instruments (in press)

A bakeable ($450^\circ C$) Geiger-Muller counter has been constructed for following chemisorption and surface reactions on small surfaces in UHV systems. The absolute efficiency of the counter is 25% for ^{14}C beta radiation which allows detection of ^{14}C -containing adsorbates on areas as small as 0.1 mm^2 .

The counter has been used in the studies of ^{14}CO chemisorption and exchange reactions on single crystals of nickel, at pressures as low as 10^{-10} torr.

4. R. P. Wei and J. D. Landes, "The Effect of D₂O on Fatigue-Crack Propagation in a High-Strength Aluminum Alloy," International Journal of Fracture Mechanics (in press)

The rates of fatigue-crack propagation for a high-strength aluminum alloy (7075-T651) in an environment of D₂O (99.98% purity) at room temperature were determined and compared with data obtained in high-purity argon and distilled water. The results showed that D₂O caused a ten-fold increase in the rate of fatigue-crack propagation (up to 10^{-4} inch per cycle), which is equal to the increase caused by distilled water. These results lend further support to the previous observation that the rate controlling process for fatigue-crack propagation in this alloy (at rates below 10^{-4} inch per cycle) is the mechanical process of creating new crack surfaces, instead of either the transport of aggressive environment to the crack-tip or diffusion of hydrogen ions into the material ahead of the crack tip.

5. R. D. Iyengar and R. Kellerman, "The Nature of Paramagnetic Species Observed in Ammonia-Precipitated TiO₂ Powders," Journal of Catalysis (in press)

Impurity centers, responsible for an ESR triplet ($g = 1.980, 2.002$ and 2.024) observed on oxygen-treated titanium dioxide, are caused by the ammonia used in preparing the samples by hydrolysis of TiCl₄. Evidence is presented to show the triplet arises from a nitrogen and oxygen-containing species which is formed from ammonia during high-temperature drying or oxygen treatment.

6. R. P. Wei, "Some Aspects of Environment-Enhanced Fatigue-Crack Growth," to be published in Journal of Engineering Fracture Mechanics

Metal fatigue as an engineering problem has been well recognized. Many experiments have been carried out in recent years to assess the

effects of load amplitude, mean load, load range and test frequency on the rate of fatigue-crack growth in an attempt to characterize material response to different load profiles and to develop crack-growth 'laws' for estimating service behavior of structural components. Recent studies have shown that fatigue-crack growth can be influenced strongly by the test environment, the effect being dependent on the particular material-environment involved. These results suggest that a reinterpretation of the data of previous studies and a careful reassessment of the various 'laws' will be required. Hence, a critical review and analysis of existing fatigue-crack-growth data on high-strength aluminum and titanium alloys and high-strength steels have been made. The influences of load profile, test frequency, temperature, test environment and state-of-stress on fatigue-crack growth are discussed. Correlation with environment-enhanced crack growth under sustained loads is examined. Possible mechanisms, synergistic effects and implications regarding fatigue-crack-growth 'laws' are considered.

7. Henry Leidheiser, Jr., "Basic Studies of Surface Phenomena and Their Relation to Corrosion," to be published in an ASTM Special Technical Publication

Basic studies of surface phenomena should be carried out on samples of known composition, surface smoothness, and surface structure. The use of single crystals of known orientation in combination with ultrahigh vacuum is one of the more useful techniques. Types of information obtainable from experiments using single crystals are summarized with emphasis on the relationship of such studies to practical corrosion problems. A summary is given of recent work carried out by Professor Klier at Lehigh University on the interaction of ^{14}CO with single crystals of nickel of known orientation. This technique offers promise for quantitatively characterizing the cleanliness of nickel surfaces, since the amount of adsorption is reduced as the surface is contaminated with oxide.

Naval Research Laboratory

1. D. A. Meyn, "The Nature of Fatigue-Crack Propagation in Air and Vacuum for 2024 Aluminum," ASM Transactions Quarterly, Vol. 61, No. 1, March 1968, pp. 52-61

Cyclic fatigue-crack propagation studies on 2024 aluminum were conducted to elucidate the mechanism of crack growth. The propagation rate ($\Delta a/\Delta N$) in air at relatively low amplitudes was found to be three times that in a vacuum of 1 to 3×10^{-6} torr, for a given stress intensity amplitude (ΔK_I). The crack propagation rates in the two environments tended to become similar at the highest amplitudes studied, where $\Delta a/\Delta N \sim 0.3 \mu/\text{cycle}$ and $\Delta K_I \sim 15,000 \text{ psi}/\sqrt{\text{in.}}$. The fracture surfaces of specimens fatigued in vacuum were quite different from the fracture surfaces of those fatigued in air. The former had no verifiable fractographic fatigue striations and were of an irregular and wrinkled appearance. The large facets in the fracture surfaces of coarse-grained specimens fatigued in air were all within 20° of $\{001\}$, and the majority within 10° of $\{001\}$. Facets in fracture surfaces of similar specimens fatigued in vacuum were of two types. Type A facets were always nearly perpendicular to the stress axis and were of $\{001\}$ orientation with a frosty appearance similar to the vacuum fatigue-fracture surfaces of fine-grained specimens. Type B facets were exactly $\{111\}$, very shiny and cleavage-like, and were inclined at a steep angle to the gross fracture plane. It was concluded that at low amplitudes in air, cracking proceeded by environmental tensile cracking along $\{001\}$ with plastic deformation at the crack tip at the end of each cycle. In vacuum, the plastic relaxation process proposed by Laird was considered to be the probable mechanism.

2. Clarence M. Shepherd and Sigmund Schuldiner, "Potentiostatic Current-Potential Measurements on Iron and Platinum Electrodes in High-Purity Closed Alkaline Systems," J. Electrochem. Soc. 115, 1124 (1968); NRL Report 5203, April 30, 1968

Potentiostatic polarization curves were determined for Fe, Pt, and combinations of Fe and Pt electrodes in NaOH and LiOH solutions saturated with helium. With the high-purity, gas-tight system used, the level of reactable impurities was reduced to about 10^{-6} ppm. Under these conditions the primary reactions are, depending on potential, the oxidation or reduction of OH^- and water. Iron does not significantly corrode or show a decrease in reaction rate with an increase in potential (passivate). Iron with its surface layer acts like an inert noble metal similar to platinum. Chloride ion causes extensive iron corrosion and completely changes the potentiostatic polarization behavior and does cause typical passive behavior. Under high-purity conditions, iron is an excellent catalyst for the hydrogen oxidation reaction; the presence of chloride ion, however, almost completely destroys the catalytic properties of Fe for this reaction. Unreactable and unremovable impurities such as carbonate, silicate, sulfate, etc., apparently do not have major effects on the polarization behavior of Fe. The major anion, OH^- , appears to dominate the inert anion effects.

3. D. G. Howe and R. J. Goode, "Effects of Heat Treating Environmental Conditions on the Stress-Corrosion Cracking Resistance of Several Titanium Alloys," ASTM STP No. 432, 1968, pp. 189-201

The effects of heat treating environmental conditions on the stress-corrosion-cracking resistance of several titanium alloys have been studied. The alloys studied in this investigation were the Ti-8Al-1Mo-1V, Ti-7Al-1Mo-1V, Ti-6Al-4V, and Ti-7Al-2.5Mo alloys. Precracked cantilever

type specimens were heat treated in either an inert atmosphere or in vacuum and tested in a 3.5 per cent salt water solution. A comparison of the stress intensity required for failure in salt water with that required for "dry" mechanical fracture indicates that all of these alloys become essentially insensitive to the aqueous environment when vacuum solution annealed and helium gas cooled. Similar heat treatments in argon or helium developed a wide range in level of stress-corrosion-cracking resistance for these alloys; the level was dependent upon the temperatures used. The environmental conditions associated with aging treatments at 1200 F following the solution anneal appear to have little effect on the stress-corrosion-cracking resistance of these alloys. Comparison of the stress-corrosion cracking data with hydrogen content before and after treatment indicates a close connection between stress-corrosion cracking sensitivity and hydrogen content in the material even at very low hydrogen levels. These results suggest that hydrogen contained in the metal may play an important role in the stress-corrosion cracking process of titanium alloys.

4. B. F. Brown, C. T. Fujii, and E. P. Dahlberg, "Methods for Studying the Solution Chemistry Within Stress-Corrosion Cracks," to be published in Journal of Electrochemical Society

A method has been developed to freeze advancing stress-corrosion cracks and to open them for analysis of the corrodent near the advancing crack tip. Aluminum alloys 7075 and 7079 and high-strength steels showed a pH in the region of propagation of about 3.7 or possibly somewhat less, and for titanium-aluminum alloys the pH was about 1.5; the original bulk corrodent was nearly neutral 3.5% NaCl. Ferrous iron but no ferric iron was found in the corrodent in the case of high purity unalloyed carbon steel and nickel steel, but both ferrous and ferric ions were

found in the instance of a high purity 12% Cr steel. Soluble aluminum was found near the growing crack tip in 8-1-1 Ti alloy.

These observations make it difficult to sustain a mechanism for stress-corrosion cracking which involves oxide formation within a propagating crack.

5. B. F. Brown, "Coping with the Problem of the Stress-Corrosion Cracking of Structural Alloys in Sea Water," Journal of Ocean Engineering, publication pending

In the area of developing ocean technology, the focus of concern with respect to corrosion has shifted from general wastage to critically localized corrosion. As increasingly stronger alloys are used in sea water, one of the most important forms of critical corrosion is stress-corrosion cracking. Methods for quantifying this property are discussed, and the implications of the measured quantities to materials selection are indicated.

6. D. A. Meyn and G. Sandoz, "Fractography and Crystallography of Subcritical Crack Propagation in High Strength Titanium Alloys," submitted to Transactions of the AIME

The fracture surfaces of specimens of titanium alloys which exhibited susceptibility to subcritical crack growth in a wide variety of environments, including aqueous solutions, alcohols, hydrocarbon gases, carbon tetrachloride, and dry air, were examined. The dominant and characteristic fracture mode was cleavage, which becomes mixed with an increasing proportion of ductile fracture modes (dimples, etc.) as the applied K_I was increased. The cleavage plane in all the alloys was oriented at 15° from (0001) of the alpha phase. No indices could be assigned to the 15° cleavage plane because of uncertainty as to which zone it belonged to.

7. R. L. Patterson, Jr. and L. B. Lockhart, Jr., "The Adsorption of Carbon-14 Labeled Stearic Acid on Soda-Lime Glass," submitted as an NRL Report, December 1968

Procedures have been devised for producing highly compacted monomolecular layers of carbon-14 tagged stearic acid on fire-polished soft (soda lime) glass through retraction from nitrobenzene solution. While thermal desorption studies indicated a small quantity of weakly bonded stearic acid on the surface, its rate of removal by other mechanisms (dissolution, isotopic exchange) suggests that only a single type of bonding exists. The rate of loss of stearic acid-1-C¹⁴ increased with increasing temperature but the scatter in the data prevented the calculation of the activation energy for desorption.

Difficulties in defining the surfaces under investigation rather than weaknesses in the radiochemical technique are the major handicaps in applying radiotracers to the study of surface chemical phenomena.

B. CHRONOLOGICAL LISTING OF ARPA-GENERATED
REPORTS NOTICED IN PREVIOUS QUARTERLIES†

The Boeing Company

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3. J. C. Williams, "Some Observations on the Stress-Corrosion Cracking of Three Commercial Titanium Alloys," Document D6-19553, The Boeing Company, September 1967; ASM Trans. Quar., 60, No. 4, 646 (December 1967)
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Naval Research Laboratory

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19. D. A. Meyn, "Effect of Crack Tip Stress Intensity on the Mechanism of Stress-Corrosion Cracking of Titanium-6Al-4V in Methanol," Corrosion Science, 7, No. 10, 721-723 (October 1967)
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C. ABSTRACTS OF RELATED ARTICLES ON
STRESS-CORROSION CRACKING

1. C. D. Kim and A. W. Loginow, "Techniques for Investigating Hydrogen-Induced Cracking of Steels with High Yield Strength," Corrosion, Vol. 24, No. 10, October 1968, pp. 313-318

As part of a long range study to develop grades of steel with improved resistance to hydrogen-induced cracking, techniques for measuring hydrogen uptake and hydrogen permeability were investigated and these parameters were correlated with resistance to hydrogen-induced cracking at different strength levels. The steel used for these studies was a Ni-Cr-Mo steel heat treated to four yield strength values ranging from 95 ksi to 150 ksi. The environment studied was a hydrogen sulfide saturated aqueous solution of 3% sodium chloride and 0.5% acetic acid. The technique used to measure hydrogen permeability consisted of exposing one side of a steel specimen to the sulfide environment and electrochemically measuring the hydrogen permeating to the opposite side. Hydrogen uptake was measured by the vacuum extraction method with specimens exposed to the environment for various time periods. The results of this comparison showed that both the resistance to cracking and the apparent diffusivity of hydrogen decreased as the yield strength was increased. Hydrogen uptake increased with increasing yield strength but the steady state permeation rate was not affected by strength level. A concept of hydrogen trapping is proposed to explain the observed relationships among the parameters studied and the mechanical strength of the steel.

2. A. R. C. Westwood, C. M. Preece, and D. L. Goldheim, "Adsorption-Sensitive Mechanical Behavior," Technical Report 68-6c, Contract No. Nonr-4162(00), RIAS, Martin Marietta Corporation, March 1968

It has been suggested that certain types of adsorption-sensitive mechanical behavior may be understood, in a general way, by considering the type, concentration, mobility and adsorption-induced redistribution of the charge carriers in the solid. In this paper, some recent experimental observations by the authors on the embrittlement of solid metals by pure and alloyed liquid metals, the complex-ion embrittlement of AgCl, and Rebinder effects (adsorption-induced reductions in microhardness) in ionic crystals are described and discussed in terms of this hypothesis.

3. John R. Ambrose and Jerome Kruger, "The Stress-Corrosion of Ti and Ti-8Al-1Mo-1V in Methanol Vapour," Corrosion Science, Vol. 8, No. 3, March 1968, pp. 119-124

An investigation into the SCC of Ti and Ti-8Al-1Mo-1V in methanol has shown that failure will occur in the methanol vapour phase with times to failure being at least an order of magnitude shorter than previously reported. Those effects which significantly altered time to failure were system volume, metal surface condition, and environment composition.

4. A. H. Freedman, "Development of an Accelerated Stress-Corrosion Test for Ferrous and Nickel Alloys," Report NOR 68-58, Contract No. NAS 8-20333, Northrop Corporation, Hawthorne, California, April 1968

A simple, accelerated, laboratory test for evaluating the stress-corrosion susceptibility of a ferrous or nickel-base alloy has been developed in this program. Single-edge-notched and fatigue-cracked specimens are tension loaded in a NaCl solution (200gm/liter distilled water), and the threshold stress intensity for stress corrosion

(K_{ISCC}) is determined. Identical specimens were tension loaded in racks exposed at the seacoast, and their K_{ISCC} values were measured to act as standards for evaluating the accelerated test.

The materials investigated were Inconel 718 and the following steels in one or more conditions of heat treatment: H-11 (air melted and vacuum melted), 4340, AM355, 18Ni Maraging (250 grade), 410SS, 304SS, and 17-4PH. Weld fusion zones and synthetic heat-affected zones of the 4340, AM355, and 18Ni Maraging steels were also tested. A specimen thickness of 1/4 inch was adequate to maintain plane-strain loading at the threshold stress intensity for stress corrosion except for Inconel 718, 304SS, 17-4PH (H1150), and 410SS (1125F).

The accelerated test requires a maximum test time of 1000 hours. Test times are one to three orders of magnitude shorter than those required for similar specimens in a seacoast environment. The acceleration of test time is produced by the aggressive corrodent, the presence of a crack, and the plane-strain loading conditions.

Twenty of the twenty-three combinations of material, heat treatment, and welding conditions that were tested showed good-to-excellent agreement between the K_{ISCC} values obtained in seacoast and in accelerated tests. For H-11(AM) 1000F and 4340 800F the accelerated test is more severe than seacoast exposure and, therefore, conservative. Only AM355 SCT850(FH) has an appreciably lower K_{ISCC} for seacoast tests than is found by the accelerated test. AM355 in three other conditions of heat treatment gave good-to-excellent agreement between the two types of test.

5. J. J. Demo, "Effect of Inorganic Contaminants on the Corrosion of Metals in Chlorinated Solvents," Corrosion, Vol. 24, No. 5, May 1968, pp. 139-149

In tests on unstabilized chlorinated solvents, corrosion rates for common materials of construction were high in the condensing area when both dissolved water and HCl, a degradation product, exceeded critical low concentrations. In tests where corrosion in the condensate was severe, corrosion rates in the boiling solution were very low because concentrations of dissolved water were below a critical low value. For low rates in both solution and condensing areas, HCl and water content should be kept below 40 and 200 ppm, respectively. Use of stabilizers and selection of materials to minimize corrosion are described also.

6. N. A. Tiner, T. L. MacKay, S. K. Asunmaa, and R. G. Ingersoll, "Use of Electron Microautoradiography for Evaluating Microsegregation of Hydrogen in Titanium Alloys," ASM Transactions Quarterly, Vol. 61, No. 2, June 1968, pp. 195-202

Microsegregation of hydrogen in titanium alloys was evaluated by the use of a new microautoradiography technique. The radioactive isotope of hydrogen (tritium) was introduced into the alloys and its segregation in the beta phase was determined. The details of the technique are discussed and the microsegregation determinations made in alpha-beta, near alpha, and beta alloys are described. It was discovered that hydrogen occurred in a concentration of 200 to 300 ppm in the beta phase of the alpha-beta alloys with less than 50 ppm total hydrogen content. The use of the technique to study distribution of trace elements between microphases and their effect on the alloy properties is suggested.

7. G. Sanderson, D. T. Powell, and J. C. Scully, "The Stress-Corrosion Cracking of Ti Alloys in Aqueous Chloride Solutions at Room Temperature," Corrosion Science, Vol. 8, No. 7, July 1968, pp. 473-481

U-bend tests and dynamic straining experiments have shown that transgranular stress-corrosion cracks are formed in Ti-5 Al-2.5 Sn alloy in 3% NaCl if a fresh surface is rapidly created. This may occur on the surface of a specimen containing hydride precipitates which is plastically deformed, or at the tip of a notch. The fracture surfaces in both neutral and acidified solutions are of the same brittle character which is also found in hydrided specimens broken in air. The electrochemical and physical metallurgical factors are briefly described. It appears that the cracking is a form of slow strain-rate H embrittlement arising from the continuous pick-up of H which is discharging at the inadequately repassivated crack tip.

8. J. C. Scully, "The Electrochemical Parameters of Stress-Corrosion Cracking," Corrosion Science, Vol. 8, No. 7, July 1968, pp. 513-523

Failure to passivate of a slip step produced at the tip of a transgranular stress-corrosion crack is discussed in detail. The time for an active surface to form a passive film under stress-corrosion conditions is considered both as a function of electrode potential and as a function of the environment. Experimental evidence is cited which can be interpreted as emphasizing that Cl^- exerts a critically important delay in step passivation. The importance of ionic strength, anodic polarization, alloy compositional alterations and pH changes is considered.

9. G. Sanderson and J. C. Scully, "The Stress Corrosion of Ti Alloys in Methanolic Solutions," Corrosion Science, Vol. 8, No. 7, July 1968, pp. 541-548

Stressed specimens of Ti and its alloys suffer intergranular cracking in methanol. If the Al content is high ($\geq 5\%$) the α -phase is subject to

rapid transgranular cracking. The addition of HCl to the methanol shortens the time to failure considerably and causes a slow intergranular embrittlement, which does not require any applied stress and results in a total loss of strength in all the single phase α -alloys. This slower form of attack was not found in the $\alpha + \beta$ Ti-6Al-4V alloy. It is suggested that there are two operative processes: transgranular hydride formation and selective dissolution from α -grain boundaries. The former can occur in any environment that discharges hydrogen in reaction with Ti and that can cause breakdown of the protective film.

10. P. E. Hudson, E. S. Snavely, Jr., J. S. Payne, L. D. Fiel, and Norman Hackerman, "Absorption of Hydrogen by Cathodically Protected Steel," Corrosion, Vol. 24, No. 7, July 1968, pp. 189-196

Rates of hydrogen evolution and hydrogen absorption were determined by use of membrane experiments in environments simulating soil conditions. The objective of this work was to determine the amount of hydrogen absorbed by steel under various conditions encountered by cathodically protected pipelines. The conditions investigated included a pH range of 3 to 9, absence of and saturation by oxygen, effects of cathode poisons, and metal-to-soil potentials. For a given pipe-to-soil potential, the rate of hydrogen penetration of steel is decreased by the presence of oxygen and arsenic, and increased by the presence of sulfide.

11. F. H. Cocks, J. F. Russo, and S. B. Brummer, "The Separation of Corrosion and Stress Effects in Stress Corrosion: Ti-6Al-4V in Bromine-Methanol Solutions," Corrosion, Vol. 24, No. 7, July 1968, pp. 206-208

The time to failure for stress corrosion of Ti-6Al-4V depends strongly on the extent of pre-corrosion. Corrosion without stress is initially just as effective in causing eventual failure as is corrosion with stress; only during the last 40%

of the normal stress, corrosion life is stress critical in causing failure. Thus, only in this last stage can a stress corrosion process be said to occur. A general mechanism to account for this behavior is suggested, and a precorrosion susceptibility index is defined and used as a quantitative measure of the importance of stress at each stage of the total process leading to failure. The time to failure of Ti-6Al-4V in methanol-bromine solutions depends also on the extent of "aging" of the solution. The time to failure becomes shorter the longer the solution has been kept standing. This effect arises from the influence of the reaction products of bromine with methanol and water.

12. A. J. Sedriks and E. N. Pugh, "Effects of Environment on the Fracture Behavior of Titanium and its Alloys," Technical Report 68-11c, Contract No. DAAG46-67-C-0138(X), RIAS, Martin Marietta Corporation, August 1968

A study has been made of the mechanisms of stress-corrosion cracking (SCC) of titanium and Ti-Al alloys in methanol-iodine solutions. The path of cracking was found to depend on the composition of the alloy. In pure titanium and a Ti-2.09 w/o Al alloy SCC is intergranular. In higher alloys (>5 w/o Al) only the initial part of the crack is intergranular, the later formed transgranular propagation stage exhibiting cleavage markings.

Comparative studies of corrosion behavior, characteristics of SCC, and metallurgical factors (i.e. alloy composition and deformation characteristics) have indicated that two mechanisms may be operative. The intergranular SCC process appears to involve stress-accelerated corrosion, while the transgranular process exhibits the characteristics of cleavage and appears to be related to a reduced propensity for cross-slip. Comparison of the SCC behavior in methanol-iodine solutions with that in a methanol-hydrochloric acid solution indicates that similar processes are operative in the latter solution.

13. D. I. Phalen and D. A. Vaughan, "The Role of Surface Stress on Hydrogen Absorption by 4340 Steel," Corrosion, Vol. 24, No. 8, August 1968, pp. 243-246

The reaction kinetics of stressed, high strength steel with cathodically generated hydrogen are shown to follow the first-order rate equation, with rate constant $k = -5 \times 10^5 \exp [-9700/RT]$ in which the activation energy is equivalent to that for diffusion of hydrogen in iron. The pre-exponential constant, however, is several orders of magnitude greater than that obtained for diffusion and is discussed in terms of the number of reactive sites. While the number of incipient sites is believed to be comparable to the number of subgrain (domain) boundaries in martensity (10^{12} cm^{-2}), a stress of 85 ksi activates approximately 10^7 sites/ cm^2 . These sites are not activated by a surface tensile stress of less than 40 to 50 ksi. When these sites are activated, however, hydrogen diffuses to the area of higher tensile stress. In the case of ferritic structure, the hydrogen reaction rate does not increase with the magnitude of the tensile stress.

14. C. D. Kim and A. W. Loginow, "Techniques for Investigating Hydrogen-Induced Cracking of Steels with High Yield Strength," Corrosion, Vol. 24, No. 10, October 1968, pp. 313-318

As part of a long range study to develop grades of steel with improved resistance to hydrogen-induced cracking, techniques for measuring hydrogen uptake and hydrogen permeability were investigated and these parameters were correlated with resistance to hydrogen-induced cracking at different strength levels. The steel used for these studies was a Ni-Cr-Mo steel heat treated to four yield strength values ranging from 95 ksi to 150 ksi. The environment studied was a hydrogen sulfide saturated aqueous solution of 3% sodium chloride and 0.5% acetic acid. The technique used to measure hydrogen permeability consisted of exposing one side of a steel specimen to the sulfide environment and electrochemically measuring the hydrogen permeating to the

opposite side. Hydrogen uptake was measured by the vacuum extraction method with specimens exposed to the environment for various time periods. The results of this comparison showed that both the resistance to cracking and the apparent diffusivity of hydrogen decreased as the yield strength was increased. Hydrogen uptake increased with increasing yield strength but the steady state permeation rate was not affected by strength level. A concept of hydrogen trapping is proposed to explain the observed relationships among the parameters studied and the mechanical strength of the steel.

15. J. Flis and J. C. Scully, "The Role of Interstitial and Substitutional Impurities in Stress Corrosion Cracking of Low Carbon Steel in Nitrate Solution," Corrosion, Vol. 24, No. 10, October 1968, pp. 326-334

The metallurgical aspects of the stress corrosion cracking of Fe-0.025%C in 5N NH_4NO_3 at 75C (167F) have been investigated. Sites of preferential corrosion in the alloy [annealed at 925C (1697F) and aged at 250C (482F)] were examined by transmission electron microscopy, and the susceptibility of the alloy to stress corrosion cracking after varying heat treatment was examined in constant strain rate tests. From the experimental data and calculated rate of transfer of impurities to and from grain boundaries, it was concluded that the tendency of grain boundaries to preferential corrosion is determined primarily by segregated substitutional constituents, and not by C or N.

16. J. C. Scully, "The Mechanical Parameters of Stress-Corrosion Cracking," Corrosion Science, Vol. 8, No. 10, October 1968, pp. 759-769

The effect of notches upon the mechanical properties of a metal specimen is discussed. In particular, the mechanical parameters required to create large areas of metal at the tip of a crack too rapidly for the environment to repassivate are considered in detail. Plane strain sub-critical

crack growth is of considerable importance in this respect. The use of the stress intensity factor and the strain-energy release rate in determining the fracture mechanism is discussed with reference to the stress-corrosion of α -brass, Ti and Al alloys and high strength steels. The role of strain-rate, grain size and cold work is briefly considered with reference to three categories of cracking arising from (a) anodic dissolution, (b) H embrittlement, and (c) tarnish film rupture.

17. G. Sanderson and J. C. Scully, "The Hot Salt Cracking of Ti Alloys," Corrosion Science, Vol. 8, No. 10, October 1968, pp. 771-777

Hot salt cracking of Ti alloys has been investigated by examining the reaction of hot Cl_2 with some α phase alloys: Ti-5Al-2.5Sn and binary alloys of Ti-Al and Ti-Sn. Cl_2 can cause intergranular cracking in bulk specimens of the alloys if only a narrow, highly strained region is exposed. Thin foil electron microscope experiments have shown that Cl_2 preferentially attacks dislocation lines and grain boundaries in the susceptible alloys. The solute elements segregated to these regions stimulate the formation of TiCl_2 which is probably the main corrosion reaction. The role of O_2 and moisture both in crack initiation and propagation is briefly considered.

D. DIARY OF EVENTS

Professor R. D. Townsend, Carnegie-Mellon University, gave a series of four lectures on the subject of age hardening and stress-corrosion cracking in aluminum alloys at the Naval Research Laboratory on 26 November 1968.

The quarterly meeting for the ARPA coupling program was held at Carnegie-Mellon University on 3 December 1968. The meeting was devoted to technical discussions of stress-corrosion cracking in steels. Some 35 people both from within and outside the ARPA program were in attendance.

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13. ABSTRACT <p>This report contains a compilation of abstracts from recently published reports and journal articles generated under the ARPA Coupling Program on Stress-Corrosion Cracking, ARPA Order 878. The abstracted reports are from work done at Carnegie-Mellon University, Lehigh University, Georgia Institute of Technology, The Boeing Company, and the Naval Research Laboratory. Selected abstracts of articles from outside the ARPA program in the field of stress-corrosion cracking and a diary of events are also included.</p>			

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